

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 021 682 B1**

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
06.03.2002 Bulletin 2002/10

(51) Int Cl.7: **F23C 11/00**

(21) Application number: **98951522.6**

(86) International application number:
PCT/EP98/06522

(22) Date of filing: **08.10.1998**

(87) International publication number:
WO 99/18392 (15.04.1999 Gazette 1999/15)

(54) **FLAMELESS COMBUSTOR PROCESS HEATER**

HEIZVORRICHTUNG MIT FLAMMENLOSER VERBRENNUNG

DISPOSITIF DE CHAUFFAGE COMPRENANT UNE CHAMBRE DE COMBUSTION SANS FLAMME

(84) Designated Contracting States:
**AT BE CH DE DK ES FI FR GB GR IE IT LI LU NL
PT SE**

(30) Priority: **08.10.1997 US 62439**

(43) Date of publication of application:
26.07.2000 Bulletin 2000/30

(73) Proprietor: **SHELL INTERNATIONALE
RESEARCH MAATSCHAPPIJ B.V.
2596 HR Den Haag (NL)**

(72) Inventors:
• **MIKUS, Thomas**
Houston, TX 77077 (US)
• **SHAH, Rashmi, K.**
Houston, TX 77071 (US)

(56) References cited:
US-A- 4 104 018 **US-A- 5 154 599**
US-A- 5 255 742

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 1 021 682 B1

Description

FIELD OF THE INVENTION

[0001] The invention relates to a process heater for high temperature reactions with improved control of heat transfer.

BACKGROUND TO THE INVENTION

[0002] High temperature, typically endothermic, reactions such as steam methane reforming to form hydrogen from steam and hydrocarbons, and pyrolysis of hydrocarbons to produce olefins are typically carried out in furnace tubes with direct fired radiant heat transfer to the outside surface of the tubes, and flowing reactants on the inside of the tubes. Direct fired heat is often beneficial because of the high temperature level of heat required, high heat flux required, and relatively low capital cost of the furnace. But it is difficult to maintain uniform heat transfer in a fired furnace. Therefore, these furnace tube must be operated at an average tube skin temperature that is somewhat below the maximum allowable tube skin temperature because of variations in the tube skin temperatures. This variation is compounded by difficulty in measuring these temperatures. Controlling maximum temperatures is important because coke will generally develop more rapidly on the tube-side at hotter spots. Thicker coke imparts increased resistance to heat transfer, and causes the hot spot to become hotter. This effect snow-balls, and can result in failure of the tube if not detected and corrective action taken. The corrective action is typically to decrease firing of one or more burners in the vicinity of the hot spot. Decreasing firing then lowers heat transfer around the hot spot, and generally is detrimental to performance of the heater.

[0003] Lengths of tubes in fired furnaces are also generally limited due to physical constraints. In some steam-methane reforming furnaces multiple levels of burners are provided in order to distribute radiant heat more evenly to the tubes, but even with multiple levels of burners, the vertical distance over which burners can be provided is limited because of the difficulty of providing fuel and air distribution with varying amounts of draft in the furnace. Thus, when a long flowpath within a furnace is desired, multiple passes are generally provided with a plurality of elbows within the firebox. These elbows are common points of problems due to uneven flow and temperatures, and possible erosion along the inside radius.

[0004] Combustion of fuels to provide heat inherently generates nitrogen oxides ("NO_x") as a result of exposure of nitrogen, oxygen and free-radicals at elevated temperatures. In certain areas, emission of NO_x is limited, and expensive measures such as flue gas treatments such as Selective Catalytic Reduction DeNOx systems are occasionally required. Burner systems are available which reduce generation of NO_x by controlling

combustion temperatures, but the combustion temperatures are difficult to control, and even under ideal conditions, a significant amount of NO_x is generated.

[0005] Another problem with typically fired process heaters is the limited efficiency of the radiant section of the heater. Particularly if combustion air preheating is not provided, a considerably amount of the fuel burned is utilized to heat the combustion air to flame temperatures. Even when combustion air preheat is provided, the combustion air preheat typically does not bring the temperature of the combustion air to near flame temperatures. Thus the radiant section efficiencies could be considerably improved with a more effective preheating of combustion air, and preheating of the fuel is typically not practiced because significant preheating can result in coke formation from the fuel.

[0006] Many methods have been suggested to cope with direct firing of reaction furnaces. Additives for feeds to pyrolysis furnaces have been proposed, including U. S. patent Nos. 5,567,305, and 5,330,970. These component are said to reduce and delay the onset of coke formation, but do not eliminate the formation of coke.

[0007] Ceramic coatings and pretreatments to furnace tube have also been suggested as being effective to reduce coking in, for example, U.S. patent Nos. 5,600,051, 5,463,159, 5,446,229, and 5,424,095. But like treatments to the feedstocks, they are only marginally effective.

[0008] Indirect heating and electrical heating has also been suggested, in for example, U.S. patent Nos. 5,559,510, 5,554,347, 5,536,488, 5,321,191, and 5,306,481 as methods to provide more even heat flux into such a reaction. These methods avoid the disadvantages of fired furnaces, but incur additional capital and/or operating costs when compared to fired furnace heaters.

[0009] Generally, yields of such reactions as reforming of hydrocarbons to produce hydrogen and carbon oxides, olefin production by pyrolysis of hydrocarbons, and styrene production are improved with increasing temperatures. It is therefore generally desirable to operate at such increased temperatures. These temperatures are generally limited by metallurgical limitations of materials that are economical and consistency of the heat transfer to the tubes.

[0010] US patent No. 4,104,018 discloses a combustor for heating a load fluid, such as a utility boiler for water, wherein a combustible mixture passes through small diameter tubes in which free flames cannot be formed and low temperature combustion occurs with low nitrogen oxide emission.

[0011] Further, flameless oxidation as a source of heat in accordance with the preamble of claims 1 and 8 is known from U.S. patent No. 5,255,742. The known flameless heater is used in a well to inject heat into a subterranean formation to recover oil therefrom.

[0012] It would be desirable to provide a process heater for use in an endothermic chemical process in which

the metallurgical limitations could be more closely approached and the chemical reaction process is optimized by maintaining a uniform heat transfer. It would be further desirable to provide such a heater which would not require excessive capital or operating costs, and which operates at a greater thermal efficiency. It would also be desirable to provide a process heater wherein generation of NO_x is greatly reduced. It would also be desirable to provide such a process heater wherein the heat can be provided to the process in a controllable fashion. Objects of the present invention therefore include accomplishing these results, and other objects which will become apparent upon examination of the following description of the invention.

SUMMARY OF THE INVENTION

[0013] These and other objects are achieved by the process heater according to claim 1 and the heating method according to claim 8.

[0014] The distributed combustion process heater of the present invention can be utilized to provide a controllable heat flux into a process chamber, from a heat source which has a uniform temperature, and very low creation of NO_x . The uniform temperatures can be utilized to increase average temperatures without exceeding maximum temperatures, or to reduce the cost of materials.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015]

Fig. 1 shows a partial sectional of a heater of the present invention.

Figs. 2 through 9 are schematics of alternative heaters of the present invention.

DESCRIPTION OF A PREFERRED EMBODIMENT

[0016] The process heater of the present invention eliminates the firebox of a conventional process heater and provides uniform heat flux at a controlled temperature level. The fire box is replaced by, for example, concentric tubes that may be in coils, or straight. Fuel and oxidant is mixed in stages and at a temperature that results in oxidation of the fuel without producing a flame, thus eliminating the flame as a radiant source of high level heat, and replaces the flame with a flowing stream of high temperature level gas. In the endothermic process, this can result in higher temperatures within metallurgical constraints, thus resulting in many processes in improved conversions, selectivities and/or yields and reduced byproduct production. Elimination of irregular temperatures also reduces risk of failures of tubulars due to local hot spots. Radiant efficiency of flameless combustion according to the present invention can also be greater, resulting in lower energy consumption.

[0017] Flameless combustion according to the present invention also avoids the high temperature levels within flames, and the free radicals that are present within the flame. This results in substantially reducing formation of NO_x compounds. NO_x levels of the present invention are less than about one hundredth of the levels of conventional fired heaters, and one tenth of the levels achievable with heaters using flames stabilized in mesh.

[0018] In some endothermic processes, multiple stages of heaters are needed in order to reheat reactants for completion of the reaction to a desired level. The present invention can be applied in such processes to continuously add heat to the reaction, resulting in a single reaction stage, and that stage being at a controlled temperature profile. This advantage can be used to significantly reduce residence time requirements, lower the pressure drop through the system, and/or decrease maximum temperatures.

[0019] Heaters of the present invention utilizing flameless combustion of fuel gas at temperature levels of about 900 °C to about 1100 °C may be fabricated from high temperature alloys such as, for example, WASSP-ALLOY, INCONEL 601, INCONEL 617, INCOLOY 800HT, HASTELLOY 235, UNIMET 500 and INCOLOY DS (WASSPALLOY, INCONEL, INCOLOY, HASTELLOY, UNIMET and INCOLOY DS are trade marks). At higher temperatures ceramic materials may be used and are preferred. Less expensive metals may be utilized in the outer conduits if internal refractor is used to limit the temperature to which such outer conduits are exposed. Ceramic materials with acceptable strength at temperatures of 900 °C to about 1400 °C are generally high alumina content ceramics. Other ceramics that may be useful include chrome oxide, zirconia oxide, and magnesium oxide based ceramics. National Refractories and Minerals, Inc., Livermore, California, A.P. Green Industries, Inc., Mexico, Missouri, and Alcoa, Alcoa Center, Penn., provide such materials.

[0020] Generally, flameless combustion is accomplished by preheating combustion air and fuel gas to above a temperature at which when the two streams are combined the temperature of the mixture exceeds the autoignition temperature of the mixture, but to a temperature less than that which would result in the oxidation upon mixing being limited by the rate of mixing. Further, the design of the fuel nozzles and oxidation chamber is such that the fuel and air velocities are high enough to blow off any stabilized flame. Recirculation or low-velocity regions where a flame could attach to the fuel nozzle are avoided. Preheating of the streams to a temperature between about 850 °C and about 1400 °C and then mixing the fuel gas into the combustion air in relatively small increments can result in flameless combustion. The increments in which the fuel gas is mixed with the combustion gas stream preferably result in about a 20 °C to 100 °C temperature rise in the combustion gas stream due to the combustion of the fuel.

[0021] In most cases, it will be preferable to mix incre-

ments of fuel as heat is removed by the process stream to accomplish a relatively uniform temperature profile, but this is not a necessary part of the present invention. For example, it may be desired to have an increasing or decreasing temperature profile. The advantage of the present invention is that the temperature profile, or flux of heat, may be controlled to be what is desired. In an exothermic process, the present invention may be used to provide a temperature profile which increases faster than the adiabatic profile.

[0022] The process chamber could contain a vapor phase process stream, a liquid phase stream, and/or a solid phase stream.

[0023] Referring to Fig. 1, a heater of the present invention is shown in a partial sectional view. An oxidation reaction chamber 1 having an inlet 2 and an outlet 3 is shown. Between the inlet and the outlet, a flowpath 4 is provided in a heat exchange relationship with a process chamber 8. A fuel conduit 5 provides a conduit for transporting fuel to nozzles 6 spaced along the flowpath 4. The nozzles are spaced so that fuel is added to the oxidation reaction chamber at a rate that results in the flow of fuel through each nozzle not resulting in a flame as the fuel mixes with the oxidation stream flowing through the flowpath of the oxidation chamber. The fuel, rather than burning with a luminous flame, will react with oxidant in a relatively uniform manner throughout the volume of the oxidation chamber. Four sets of fuel nozzles are shown, but any number of fuel nozzles may be provided, depending on the required heat flux into the process chamber. Volume of the oxidation chamber between sets of nozzles is preferably enough that the residence time of mixture is sufficient so that a significant portion of the fuel flowing through the set of nozzles is oxidized before more fuel is added.

[0024] A process chamber 8 is in heat exchange relationship to the oxidation reaction chamber 1. A process stream enters the process chamber at the inlet 11 and exits at an outlet 12. A quench heat exchanger 10 is shown to cool the process stream exiting the process chamber. A stream to be heated by the quench heat exchanger enters at quench inlet 14 and exits through quench outlet 13. The stream to be heated by the quench heat exchanger is a process inlet stream. In some processes, such as pyrolysis of hydrocarbons to produce olefins, rapid quench is desirable to reduce reactions to byproducts.

[0025] A coke inhibitor may be added to the fuel through an inhibitor injection system shown as injection line 9. The inhibitor injection line may include a control valve and a control system to ratio the inhibitor to the flow of fuel.

[0026] The fuel conduit contains a plurality of nozzles 6 (four sets shown) along the length of the oxidation reaction chamber. The nozzles provide communication between the fuel conduit and the oxidation reaction chamber. A plurality of nozzles provide for distribution of heat release within the oxidation reaction chamber.

The nozzles are sized to accomplish a the desired temperature distribution within the process chamber. A nearly even temperature profile within the process chamber is generally desired because it can result in lower maximum temperatures for a given heat flux. Because the materials of construction of the apparatus dictate the maximum temperatures, even temperature profiles will increase the heat release possible for the same materials of construction. The number of nozzles is limited only by size of nozzles which are to be used. If more nozzles are used, they must generally be of a smaller size. Smaller nozzles will plug more easily than larger nozzles. The number of nozzles is a trade-off between evenness of the temperature profile and the possibility of plugging.

[0027] The process chamber and the oxidation chamber are shown to be in concurrent flow, but may be in counter current flow, or a combination of the two, with for example, the oxidation chamber being a U-tube configuration. Such a configuration may be desirable to handle effects of differential thermal expansion of the conduits.

[0028] Catalyst may be provided in the process chamber, depending on the particular process.

[0029] A preheater 7 is shown to heat the oxidant stream to a temperature at which mixtures of the oxidant stream with fuel from the first set of nozzles will be sufficiently hot to result in flameless oxidation. The preheater may be, for example, a burner wherein fuel is mixed with some of the oxidant and burned to raise the temperature of the oxidant, or the oxidant may be preheated by heat exchange with either or both of the process chamber effluent or the oxidation reaction chamber effluent. A combination of heat exchange and then a burner may be utilized.

[0030] Alternatively, oxidant could be staged into the fuel by providing nozzles in an oxidant conduit instead of the fuel conduit, and forcing oxidant into a fuel rich stream at a temperature above the resultant mixtures.

[0031] Referring now to Fig. 2, a cross section of an alternative embodiment is shown. In this embodiment, the process chambers 8 are in tubes that are bundled together inside an insulated casing 104. The insulated casing does not need to be a pressure vessel, but reduces heat loss from the tubes which contain the reaction chambers. Fuel conduits 5 are inside of oxidation reaction chambers 1, with nozzles 6 providing communication between the two chambers.

[0032] Referring now to Fig. 3, another alternative embodiment is shown. In this embodiment, the process chambers 8 are in tubes that are bundled together inside an insulated casing 401. The insulated casing also defines the combustion chamber. Fuel conduits 5 are inside the insulated casing between the tubes that define the process chambers. The tubes defining the process chambers and the fuel conduits are shown to be relatively tightly packed, but could be spaced as necessary to provide a trade-off between pressure drop and the

size of the casing required. This alternative could approach the appearance of a shell and tube heat exchanger with baffles to space the tubes, and to channel flow of the combustion gasses back and forth across the tubes that define the process chambers.

[0033] The oxidation chamber may also be provided with an oxidation catalyst. The oxidation catalyst may be provided on a support such as alumina, or coated on the walls of the tubulars. The oxidation catalyst may be useful to expand the effective range of temperatures at which the flameless oxidation will operate with stability. The oxidation catalyst may also be useful for a start up phase prior to the oxidation chamber reaching a temperature at which the uncatalyzed oxidation reaction will proceed. Alternatively, catalyst may be effective to reduce the volume required in the oxidation chamber.

[0034] Preheating of hydrocarbon fuels to obtain flameless combustion could result in significant generation of carbon within the fuel conduit unless a carbon formation suppressant is included in the fuel stream. The carbon formation suppressant may be carbon dioxide, steam, hydrogen or mixtures thereof. Carbon dioxide and steam are preferred due to the generally higher cost of hydrogen.

[0035] Carbon is formed from methane at elevated temperatures according to the following reaction:

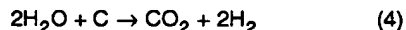
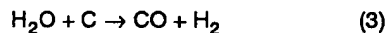


[0036] This reaction is a reversible reaction, and hydrogen functions as carbon formation suppressant by the reverse reaction.

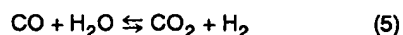
[0037] Carbon dioxide suppresses carbon formation by the following reaction:



[0038] Steam suppresses carbon formation by the following reactions:



[0039] The carbon dioxide and the carbon monoxide remain in equilibrium at elevated temperatures according to the shift gas reaction:



[0040] When the fuel is essentially methane, a molar ratio of about 1:1 of steam to methane will be sufficient

to suppress carbon formation to temperatures of about 1370°C. The molar ratios of steam to methane is preferably within the range of about 1:1 to about 2:1 when steam is utilized as the carbon formation suppressant.

5 The molar ratio of carbon dioxide to methane is preferably within the range of about 1:1 to about 3:1 when carbon dioxide is utilized as the carbon formation suppressant. The fuel preferably consists essentially of methane due to methane being more thermally stable than other
10 light hydrocarbons. The suppressant is additionally beneficial because it lowers combustion rates and reduces peak temperatures.

[0041] Need for the carbon formation suppressant may be eliminated if the fuel is not significantly preheated prior to addition to the oxidant stream, or if the residence time of any preheated fuel is sufficiently short.

[0042] Cold start-up of a heater of the present invention may utilize combustion with a flame. Initial ignition may be accomplished by injecting pyrophoric material, an electrical igniter, a spark igniter, or temporarily inserting an igniter. The heater is preferably rapidly brought to a temperature at which a flameless combustion is sustained to minimize the time period at which a flame exists. The rate of heating up the heater will typically be limited by the thermal gradients the heater can tolerate.

[0043] Flameless combustion generally occurs when a reaction between an oxidant stream and a fuel is not limited by mixing and the mixed stream is at a temperature higher than the autoignition temperature of the mixed stream. This is accomplished by avoiding high
30 temperatures at the point of mixing and by mixing relatively small increments of fuel into the oxidant. The existence of flame is evidenced by an illuminate interface between unburned fuel and the combustion products. To avoid the creation of a flame, the fuel and the oxidant are preferably heated to a temperature of between about 815 °C and about 1370 °C prior to mixing. The fuel is preferably mixed with the oxidant stream in relatively small increments to enable more rapid mixing. For example, enough fuel may be added in an increment to enable combustion to raise the temperature of the stream by about 20 °C to about 100 °C.

[0044] The process in which the heater of the present invention may be useful includes, but is not limited to: steam methane reforming, olefin production, styrene production, ammonia production, cyclohexane production, catalytic reforming of hydrocarbons, and allyl or vinyl chloride manufacture, glass or ceramic production, calcinating, reboiling of liquids in distillation, reboiling or temperature profile control in reactive distillation.

[0045] Referring now to Fig. 4, the process chamber is within combustion chamber conduits which define combustion chambers 1, and the conduits defining the combustion chambers 6 are within a larger conduit, the fuel flowing inside of the large conduit and outside of the conduits that define the oxidation chambers. Fuel nozzles 6 are located in the conduits separating the fuel from the oxidation chambers, with the fuel flowing

through the nozzles into the oxidation nozzles. The advantage of this configuration is that only one large conduit is required for fuel flow.

[0046] Referring now to Fig. 5, an alternative arrangement is shown wherein, rather than concentric tubulars, the fuel conduit 5 and the conduit defining the process chamber 8 are located within a conduit which defines an oxidation chamber 1. This configuration conveniently provides a relatively large cross sectional area or flow of combustion gases. This is desirable to reduce compression costs for the combustion gases, and also lowers the cost of the tubulars by having the largest diameter tubular also contain the lowest pressure.

[0047] Referring now to Fig. 6, an alternative similar to that shown in Fig. 5 is shown, the difference being that the fuel conduit is shown as outside of the conduit defining the combustion chamber 1. Nozzles 6 are tubular connections between the fuel conduit 5 and the tubular defining the combustion chamber 1. The advantage of this arrangement is that the fuel temperature can be limited more readily, and the need for a coke inhibition additive eliminated.

[0048] Referring now to Fig. 7, an arrangement similar to Fig. 5 is shown with an additional feature that the combustion chamber flow is split, with the inlet to the oxidation chamber 2 being near the center of the length of the oxidation chamber 8. Flow from the inlet splits into a flow going in each direction. This split oxidation chamber permits a longer process chamber flowpath for the distance of the combustion chamber flowpath, and reduces the flow in the oxidation chamber by half. Thus, the pressure drop is reduced by a factor of about eight for similar dimensions for the combustion flowpath. This can be beneficial because of the importance of compression costs in the exnomics of the process. This alternative may be desirable where it is desirable to have a relatively long straight flowpath for the process. As another alternative, the fuel conduit may be outside of the oxidation chamber as in Fig. 6.

[0049] Referring now to Fig. 8, another alternative with split flow of the oxidant stream is shown. This alternative has the oxidant in an inside pipe, and the inlet dividing in a tee into a flow going in each direction.

[0050] Referring now to Fig. 9, an embodiment of the present invention utilizing an oxidation chamber having a rectangular cross section is shown. The process chambers are pipes in a box. The rectangular oxidation chamber may be conveniently made large enough to contain a significant number of process chamber tubes 8. The process chamber tubes may be all parallel flow tubes, series flow, or combinations of parallel and series. One layer of process chamber tubes is shown, although multiple layers could be provided. When flow is at least partially in series, it may be desirable to have the inlets and the outlets in the same end and thereby reduce problems caused by thermal expansion of the tubes.

[0051] Other configuration of heat exchangers, such

as corrugated plate heat exchangers such as those disclosed in U.S. patent No. 4,029,146, incorporated herein by reference, may also be utilized. With the corrugated plate heat exchangers, either a fuel conduit may be inserted in the oxidant flow space for appropriate distribution of fuel, or a third set of flow streams may be provided for with nozzles between the spaces for flow of the fuel and for flow of the oxidant.

[0052] The oxidation chambers may be vertical, horizontal or inclined, and are preferably vertical when the process chamber contains a fixed bed catalyst.

[0053] The process heater of the present invention can be utilized in styrene production in the dehydrogenation of ethyl benzene to vinyl benzene (styrene) over a catalyst such as a promoted iron oxide-potassium oxide catalyst. This dehydrogenation can be performed, for example, between 550 °C and 680 °C, at pressures that range from four to about 20 kPa (3 psia) to 140 kPa (20 psia). Steam is added to the ethyl benzene feed to reduce the partial pressure of the hydrocarbons (thereby improving equilibrium ratios of the products), to act as a heat sink to reduce the temperature decrease due to the endothermic reaction, and to reduce coke formation by a water gas reaction. Most catalysts require steam to hydrocarbon molar ratios of about seven to ten. Liquid hourly space velocity based on the liquid feed is generally between about 0.4 to 0.5 hour⁻¹. Lower pressures are desired because of yield and catalyst stability, but higher pressures reduce the cost of compressing the product (including capital cost of the compression equipment). This is an endothermic reaction and it is desirable to perform the reaction nearly isothermally. As temperatures increase, undesirable byproducts (including coke) are produced at increasing rates, and as temperatures are decreased, yields decrease. Thus, it is desirable to operate the dehydrogenation process at nearly isothermal conditions. Benefits that could be realized by providing a more uniform temperature include reduction of the use of steam, operation at higher through puts, increasing yields and selectivity, decreasing coke make, and/or increasing the pressure of operation. Application of the present invention to dehydrogenation of ethylbenzene to styrene could be either as a heater or as a heater before the heater, although the preferred embodiment is to utilize the present invention as a heater with dehydrogenation catalyst in at least a portion of the process chamber which is heated by flameless combustion.

[0054] As a steam reforming furnace, the present invention utilizes a catalyzed process chamber to convert a hydrocarbon and steam to hydrogen, carbon monoxide and carbon dioxide. This is a highly endothermic reaction with higher temperatures favoring equilibrium of hydrogen and carbon monoxide from hydrocarbon feeds. Methane is the preferred feed for hydrogen production by steam reforming, but hydrocarbons other than methane can be utilized. The higher the molecular weights, the greater the tendency to form coke. Thus,

when feed such as naphthas are used, a higher ratio of steam to carbon is generally needed. Steam to carbon molar ratios are generally between about three and five, space velocities are generally very high, in the order of 5000 to 8000 hour⁻¹, temperatures are generally between about 800 and 870 °C, and pressures are typically between about 2 and 2.5 MPa (300 to 350 psig). Higher temperatures favor the equilibrium of hydrogen over methane, and it is typical for the heater outlet hydrogen purity to be at least at a hydrogen purity which would be at equilibrium at a temperature within 25 °F of the heater outlet temperature. The catalyst is a nickel based catalyst, and may contain potassium to inhibit coke formation.

[0055] Hydrogen production by steam reforming can be further processed by a secondary reformer to produce, for example, methanol or ammonia.

[0056] Use of the present invention in a steam reformer can result in higher average temperatures for a fixed maximum reaction chamber temperature because of the uniform distribution of heat resulting from the distributed combustion. Thus, either steam rates could be reduced, or conversion could be increased for similar tube skin temperatures.

[0057] When the present invention is utilized in a heater for thermal cracking of hydrocarbons to olefin products, reaction temperatures in the range of 775 to 950 °C and residence times of 0.1 to 0.8 seconds can be utilized. The reaction temperatures are very dependent upon the particular hydrocarbon feed, and upon the residence time. Lighter feeds, such as ethane, can be processed at higher temperatures and higher conversions. Heavier feeds, such as gas oils, required lower temperatures because of an increased tendency to form coke and other undesirable byproducts. Residence times of about 0.1 to 0.15 seconds are preferred. Dilution steam is added to the heater hydrocarbon feed to inhibit coke deposition, and to reduce the partial pressure of the hydrocarbons. The heater effluent is preferably quenched quickly because olefin selectivity is reduced by side reactions. Quench after the reaction chamber may be either by direct contact with, for example, a gas oil stream, or indirectly by heat exchange. Indirect quench is preferred because the energy could be recovered at a more useful level.

[0058] The present invention could be utilized in, for example, a distillation column reboiler, or a vacuum flash distillation feed heater. These applications often involve heating hydrocarbons to temperatures that are limited by the tendency of the hydrocarbons to form coke, and the present invention results in a more uniform transfer of heat to the hydrocarbon stream, and thus reducing maximum temperatures of the hydrocarbons within the heaters. Further, advantages such as the reduced NO_x generation are also realized.

Claims

1. A process heater comprising:

an oxidation reaction chamber (1), the oxidation reaction chamber (1) having an inlet (2) for oxidant, an outlet (3) for combustion products, and a flowpath (4) between the inlet (2) and the outlet (3);

a fuel conduit (5) capable of transporting a fuel mixture to a plurality of fuel nozzles (6) within the oxidation reaction chamber (1), each nozzle (6) providing communication from within the fuel conduit (5) to the oxidation chamber (1), with each nozzle (6) along the flowpath (4) between the inlet (2) and the outlet (3);

a preheater (7) in communication with the oxidation chamber inlet (2), the preheater (7) capable of increasing the temperature of the oxidant to a temperature resulting in the combined oxidant and fuel from the fuel nozzle (6) closest to the oxidation chamber inlet (2) being greater than the autoignition temperature of the combined oxidant and fuel from the fuel nozzle (6) closest to the oxidation chamber inlet (2), wherein the heat transferred from the oxidation section does not cause the temperature of the mixture within the oxidation reaction chamber (1) in the vicinity of each fuel nozzle (6) to decrease below the autoignition temperature of the combined mixture in the oxidation chamber (1) in the vicinity of that fuel nozzle (6), wherein the heater further comprises an endothermic reaction process chamber (8) in a heat exchange relationship to the oxidation reaction chamber (1).

2. The process heater of claim 1 further comprising a coke inhibitor injection system (9), the coke inhibitor system in communication with the fuel supply conduit (5) wherein an amount of coke inhibitor supplied can be effective to inhibit coke formation at fuel conduit (5) operating temperatures.

3. The process heater of claim 1 wherein the fuel conduit (5) is a tubular conduit essentially centrally located within the oxidation reaction chamber (1).

4. The process heater of claim 3 wherein the oxidation reaction chamber (1) is essentially centrally located within the process chamber (8).

5. The process heater of claim 1 wherein the process chamber (8) is a pyrolysis reaction chamber for the production of olefins.

6. The process heater of claim 1 wherein the process chamber (8) is effective as a steam methane re-

forming reaction chamber.

7. The process heater of claim 1 wherein the process heater is a ethylbenzene dehydrogenation heater.

8. A method to provide heat to a process by means of an oxidation reaction chamber (1), the oxidation reaction chamber (1) having an inlet (2) for oxidant, an outlet (3) for combustion products, and a flow-path (4) between the inlet (2) and the outlet (3), the method comprising the steps of:

providing a fuel;
 adding to the fuel a coke inhibition component in an amount effective to inhibit coke formation at heater operating temperatures;
 transporting a fuel mixture to a plurality of fuel nozzles (6) within the oxidation reaction chamber (1), with each nozzle (6) along the flowpath (4) between the inlet (2) and the outlet (3);
 preheating the oxidant to a temperature resulting in the combined oxidant and fuel from the fuel nozzle (6) closest to the oxidation chamber inlet (2) being greater than the autoignition temperature of the combined oxidant and fuel from the fuel nozzle (6) closest to the oxidation chamber inlet (2), wherein the method further comprises transferring heat from the oxidation reaction chamber (1) to an endothermic reaction process chamber (8) in a heat exchange relationship to the oxidation reaction chamber (1) wherein the heat transferred from the oxidation section does not cause the temperature of the mixture within the oxidation reaction chamber (1) in the vicinity of each fuel nozzle (6) to decrease below the auto ignition temperature of the combined mixture in the oxidation chamber (1) in the vicinity of that fuel nozzle (6).

9. The method of claim 8 wherein the process is a steam methane reforming process.

10. The method of claim 8 wherein the process is an pyrolysis reaction for production of olefins.

11. The method of claim 8 wherein the process is a ethylbenzene dehydrogenation process.

12. The method of claim 8 wherein the coke inhibition component is selected from the group consisting of carbon dioxide and steam.

Patentansprüche

1. Prozeßheizvorrichtung, mit:

einer Oxidationsreaktionskammer (1), wobei

die Oxidationsreaktionskammer (1) einen Einlaß (2) für Oxidationsmittel, einen Auslaß (3) für Verbrennungsprodukte und einen Strömungspfad (4) zwischen dem Einlaß (2) und dem Auslaß (3) aufweist;

einer Brennstoffleitung (5), die eine Brennstoffmischung zu einer Mehrzahl von Brennstoffdüsen (6) im Inneren der Oxidationsreaktionskammer (1) befördern kann, wobei jede Düse (6) eine Verbindung vom Inneren der Brennstoffleitung (5) zu der Oxidationskammer (1) herstellt, wobei jede Düse (6) entlang des Strömungspfad (4) zwischen dem Einlaß (2) und dem Auslaß (3) liegt;

einem Vorerhitzer (7), der in Verbindung mit dem Oxidationskammereinlaß (2) steht, wobei der Vorerhitzer (7) die Temperatur des Oxidationsmittels auf eine Temperatur erhöhen kann, die dazu führt, daß die Temperatur des kombinierten Oxidationsmittels und Brennstoffes aus der dem Oxidationskammereinlaß (2) nächstgelegenen Brennstoffdüse (6) größer als die Selbstzündungstemperatur des kombinierten Oxidationsmittels und Brennstoffes aus der dem Oxidationskammereinlaß (2) nächstgelegenen Brennstoffdüse (6) ist, wobei die vom Oxidationsabschnitt aus übertragene Wärme nicht bewirkt, daß die Temperatur der Mischungen im Inneren der Oxidationsreaktionskammer (1) in der Nähe jeder Brennstoffdüse (6) unter die Selbstzündungstemperatur der kombinierten Mischung in der Oxidationskammer (1) in der Nähe jener Brennstoffdüse (6) sinkt, wobei die Heizvorrichtung ferner eine endotherme Reaktionsprozeßkammer (8) aufweist, die in einer wärmetauschenden Beziehung zu der Oxidationsreaktionskammer (1) steht.

2. Heizvorrichtung nach Anspruch 1, ferner mit einem Verkokungsinhibitor-Einspritzsystem (9), wobei das Verkokungsinhibitorsystem in Verbindung mit der Brennstoffzufuhrleitung (5) steht, wobei eine Menge des zugeführten Verkokungsinhibitors wirksam sein kann, um die Koksbildung bei den Betriebstemperaturen der Brennstoffleitung (5) zu verhindern.

3. Prozeßheizvorrichtung nach Anspruch 1, bei welcher die Brennstoffleitung (5) eine Rohrleitung ist, die im wesentlichen zentral im Inneren der Oxidationsreaktionskammer (1) liegt.

4. Prozeßheizvorrichtung nach Anspruch 3, bei welcher die Oxidationsreaktionskammer (1) im wesentlichen zentral im Inneren der Prozeßkammer (8) liegt.

5. Prozeßheizvorrichtung nach Anspruch 1, bei welcher die Prozeßkammer (8) eine Pyrolysereaktionskammer zur Produktion von Olefinen ist.
6. Prozeßheizvorrichtung nach Anspruch 1, bei welcher die Prozeßkammer (8) als Dampf-Methan-Reformierungsreaktionskammer wirkt.
7. Prozeßheizvorrichtung nach Anspruch 1, bei welcher die Prozeßheizvorrichtung eine Ethylbenzol-Dehydrierungs-Heizvorrichtung ist.
8. Verfahren zum Zuführen von Wärme zu einem Prozeß mit Hilfe einer Oxidationsreaktionskammer (1), wobei die Oxidationsreaktionskammer (1) einen Einlaß (2) für Oxidationsmittel, einen Auslaß (3) für Verbrennungsprodukte und einen Strömungspfad (4) zwischen dem Einlaß (2) und dem Auslaß (3) aufweist, wobei das Verfahren die Schritte umfaßt:

Zurfügungstellen eines Brennstoffes;

Zugeben einer Verkokungsinhibitorkomponente zu dem Brennstoff in einer Menge, die wirksam ist, um bei den Betriebstemperaturen der Heizvorrichtung eine Koksbildung zu verhindern;

Befördern einer Brennstoffmischung zu mehreren Brennstoffdüsen (6) im Inneren der Oxidationsreaktionskammer (1), wobei jede Düse (6) entlang des Strömungspfades (4) zwischen dem Einlaß (2) und dem Auslaß (3) liegt;

Vorerhitzen des Oxidationsmittels auf eine Temperatur, die dazu führt, daß die Temperatur des kombinierten Oxidationsmittels und Brennstoffes aus der dem Oxidationskammereinlaß (2) nächstgelegenen Brennstoffdüse (6) größer als die Selbstzündungstemperatur des kombinierten Oxidationsmittels und Brennstoffes aus der dem Oxidationskammereinlaß (2) nächstgelegenen Brennstoffdüse (6) ist, wobei das Verfahren ferner das Übertragen von Wärme von der Oxidationsreaktionskammer (1) zu einer endothermen Reaktionsprozeßkammer (8) umfaßt, die in einer wärmetauschenden Beziehung zu der Oxidationsreaktionskammer (1) liegt, wobei die vom Oxidationsabschnitt aus übertragene Wärme nicht bewirkt, daß die Temperatur der Mischung im Inneren der Oxidationsreaktionskammer (1) in der Nähe jeder Brennstoffdüse (6) unter die Selbstzündungstemperatur der kombinierten Mischung in der Oxidationskammer (1) in der Nähe jener Brennstoffdüse (6) absinkt.

9. Verfahren nach Anspruch 8, bei welchem der Pro-

zeß ein Dampf-Methan-Reformierungsprozeß ist.

10. Verfahren nach Anspruch 8, bei welchem der Prozeß eine Pyrolysereaktion für die Produktion von Olefinen ist.
11. Verfahren nach Anspruch 8, bei welchem der Prozeß ein Ethyl-Benzol-Dehydrierungsprozeß ist.
12. Verfahren nach Anspruch 8, bei welchem die Verkokungsinhibitorkomponente aus der Gruppe bestehend aus Kohlendioxid und Dampf ausgewählt wird.

Revendications

1. Réchauffeur de traitement comprenant :

une chambre de réaction d'oxydation (1), la chambre de réaction d'oxydation (1) comportant une entrée (2) pour un oxydant, une sortie (3) pour des produits de combustion et un parcours d'écoulement (4) entre l'entrée et la sortie (3);

un conduit de combustible (5) pouvant transporter un mélange combustible vers une pluralité d'injecteurs de combustible dans la chambre de réaction d'oxydation (1), chaque injecteur apportant une communication de l'intérieur du conduit de combustible (5) à la chambre d'oxydation (1), chaque injecteur étant agencé le long du parcours d'écoulement (4) entre l'entrée (2) et la sortie (3);

un préchauffeur (7) en communication avec l'entrée de chambre d'oxydation (2), le préchauffeur (7) pouvant élever la température de l'oxydant à une température résultante dans l'oxydant et le combustible combinés depuis l'injecteur de combustible (6) le plus proche de l'entrée de chambre d'oxydation (2) plus élevée que la température d'autoallumage de l'oxydant et du combustible combinés depuis l'injecteur de combustible le plus proche de l'entrée de chambre d'oxydation (2), dans lequel la chaleur transférée de la section d'oxydation n'entraîne pas un abaissement de la température du mélange dans la chambre de réaction d'oxydation (1) à proximité de chaque injecteur de combustible (6) en dessous de la température d'autoallumage du mélange combiné dans la chambre d'oxydation (1) à proximité de cet injecteur de combustible (6), dans lequel le réchauffeur comprend de plus une chambre de traitement de réaction endothermique (8) dans une relation d'échange de chaleur avec la chambre de réaction d'oxydation (1).

2. Réchauffeur de traitement suivant la revendication 1, comprenant de plus un système d'injection d'inhibiteur de coke (9), le système à inhibiteur de coke étant en communication avec le conduit d'amenée de combustible (5) dans lequel une quantité d'inhibiteur de coke amenée peut être efficace pour empêcher la formation de coke aux températures d'utilisation du conduit de combustible (5). 5
3. Réchauffeur de traitement suivant la revendication 1, dans lequel le conduit de combustible (5) est un conduit tubulaire agencé essentiellement centralement dans la chambre de réaction d'oxydation (1). 10
4. Réchauffeur de traitement suivant la revendication 3, dans lequel la chambre de réaction d'oxydation (1) est agencée essentiellement centralement dans la chambre de traitement (8). 15
5. Réchauffeur de traitement suivant la revendication 1, dans lequel la chambre de traitement est une chambre de réaction de pyrolyse pour la production d'oléfines. 20
6. Réchauffeur de traitement suivant la revendication 1, dans lequel la chambre de traitement (8) est utilisable comme chambre de réaction de reformage de méthane à la vapeur. 25
7. Réchauffeur de traitement suivant la revendication 1, dans lequel le réchauffeur de traitement est un réchauffeur pour la déshydrogénation d'éthylbenzène. 30
8. Procédé pour apporter de la chaleur à un procédé au moyen d'une chambre de réaction d'oxydation (1), la chambre de réaction d'oxydation (1) comportant une entrée (2) pour un oxydant, une sortie (3) pour des produits de combustion et un parcours d'écoulement (4) entre l'entrée (2) et la sortie (3), le procédé comprenant les étapes suivantes : 35 40

l'apport d'un combustible;

l'addition au combustible d'un composé d'inhibition de coke en une quantité efficace pour empêcher la formation de coke aux températures d'utilisation du réchauffeur; 45

le transport d'un mélange combustible vers une pluralité d'injecteurs de combustible (6) dans la chambre de réaction d'oxydation (1), chaque injecteur (6) étant agencé le long du parcours d'écoulement (4) entre l'entrée (2) et la sortie (3); 50

le préchauffage de l'oxydant à une température résultante dans l'oxydant et le combustible combinés depuis l'injecteur de combustible (6) le plus proche de l'entrée de chambre d'oxydation (2) plus élevée que la température d'auto- 55

allumage de l'oxydant et du combustible combinés depuis l'injecteur de combustible (6) le plus proche de l'entrée de chambre d'oxydation (2), dans lequel le procédé comprend, de plus, le transfert de chaleur de la chambre de réaction d'oxydation (1) vers une chambre de traitement de réaction endothermique (8) dans une relation d'échange de chaleur avec la chambre de réaction d'oxydation (1), dans lequel la chaleur transférée de la section d'oxydation n'entraîne pas un abaissement de la température du mélange dans la chambre de réaction d'oxydation (1) à proximité de chaque injecteur de combustible (6) en dessous de la température d'autoallumage du mélange combiné dans la chambre d'oxydation (1) à proximité de cet injecteur de combustible (6).

9. Procédé suivant la revendication 8, dans lequel le procédé est un procédé de reformage de méthane à la vapeur.
10. Procédé suivant la revendication 8, dans lequel le procédé est une réaction de pyrolyse pour la production d'oléfines.
11. Procédé suivant la revendication 8, dans lequel le procédé est un procédé de déshydrogénation d'éthylbenzène.
12. Procédé suivant la revendication 8, dans lequel le composant d'inhibition de coke est choisi dans le groupe comprenant le dioxyde de carbone et la vapeur.

Fig.1.

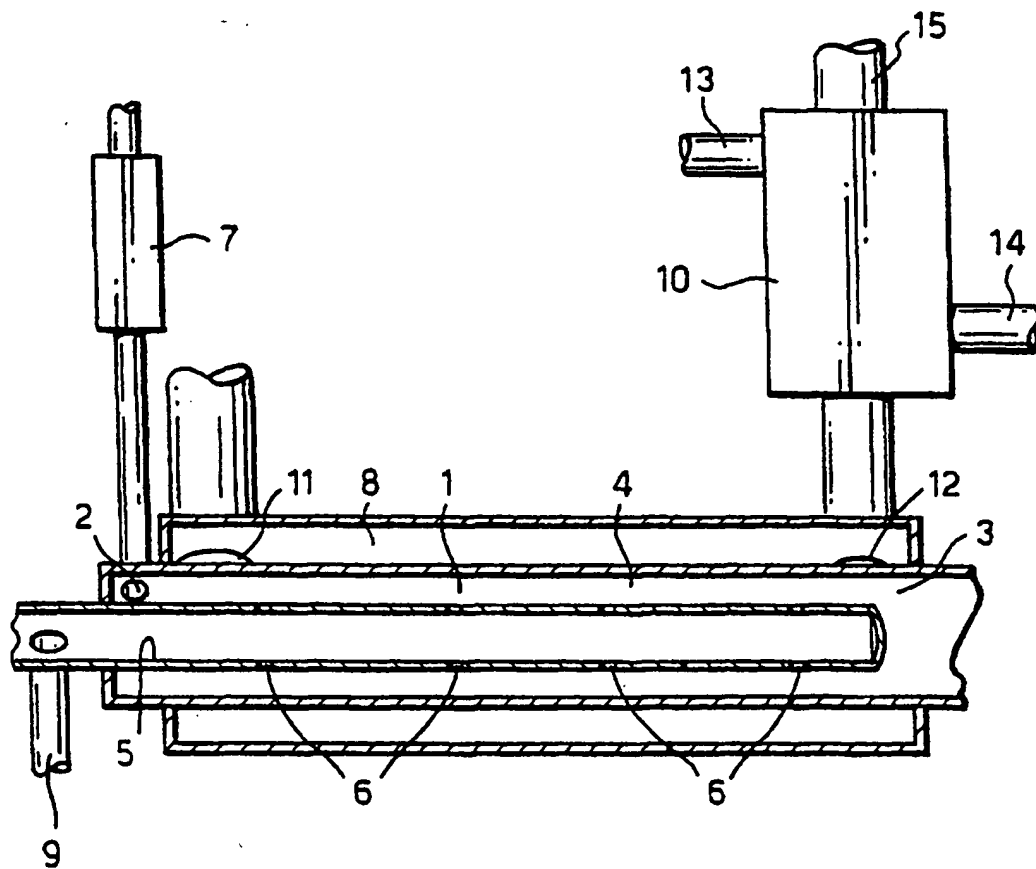


Fig.2.

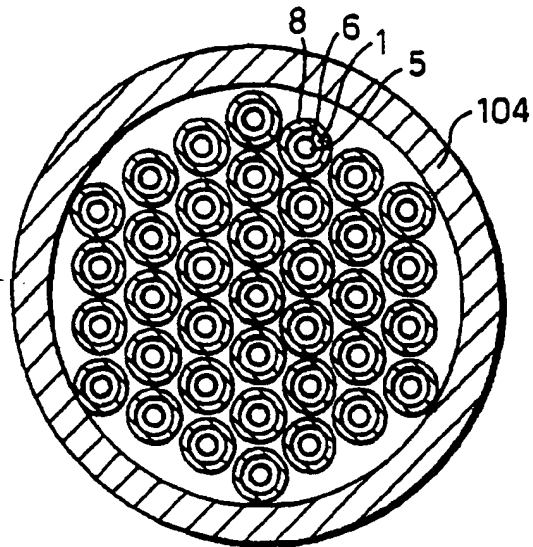


Fig.3.

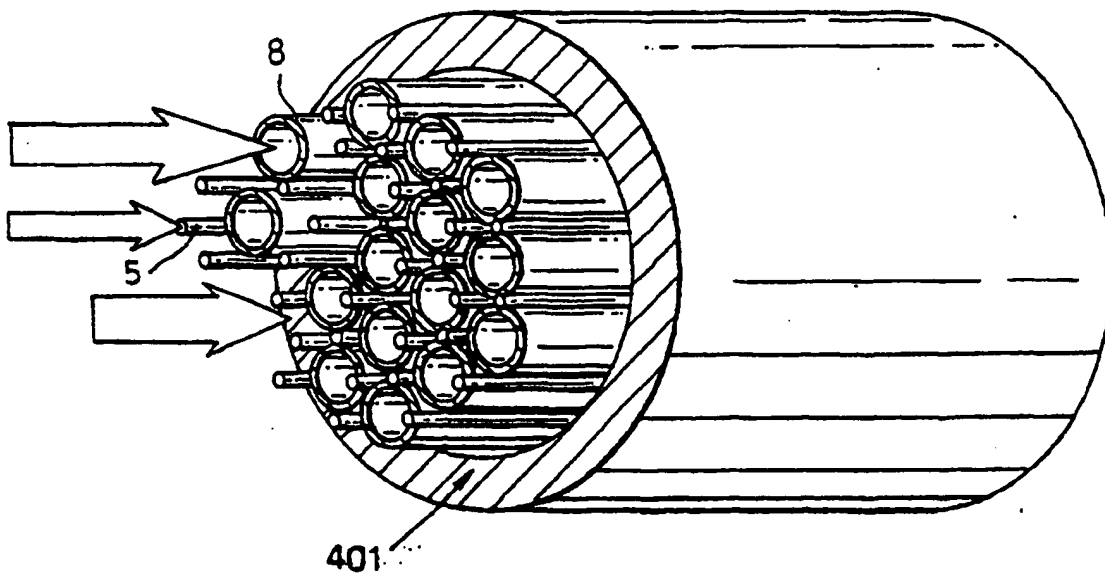


Fig.4.

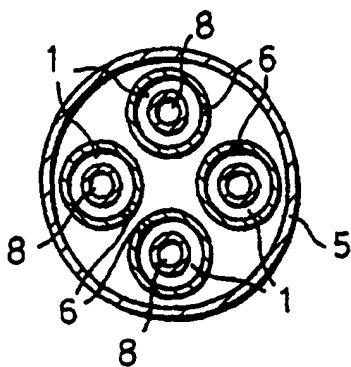


Fig.5.

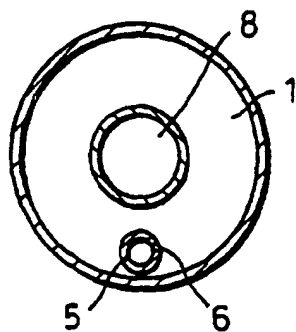


Fig.6.

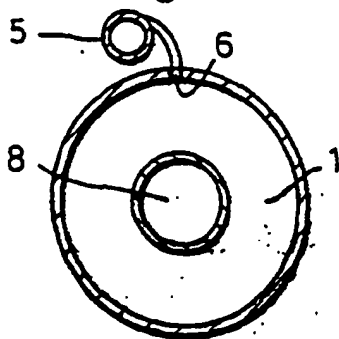


Fig.7.

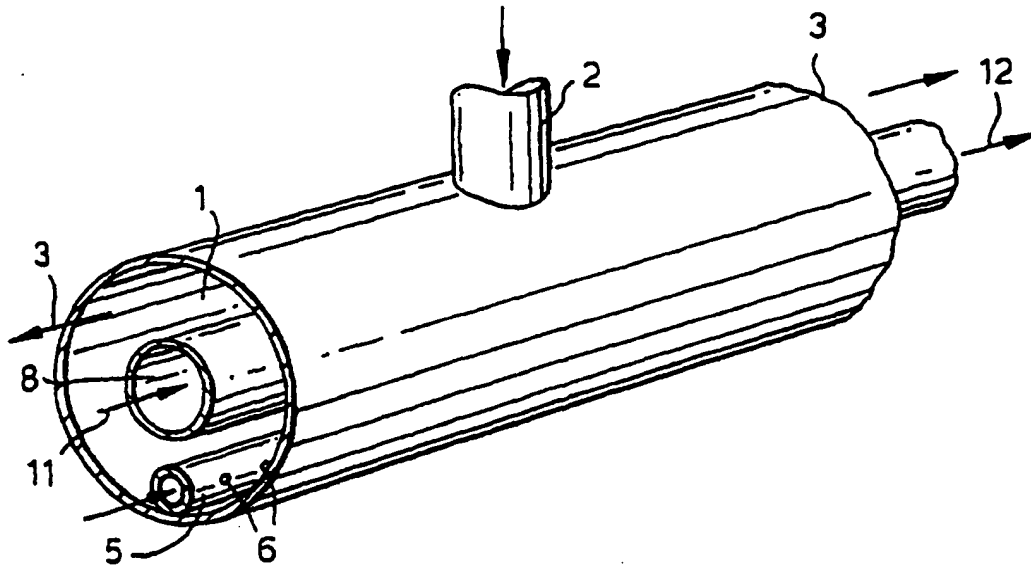


Fig.8.

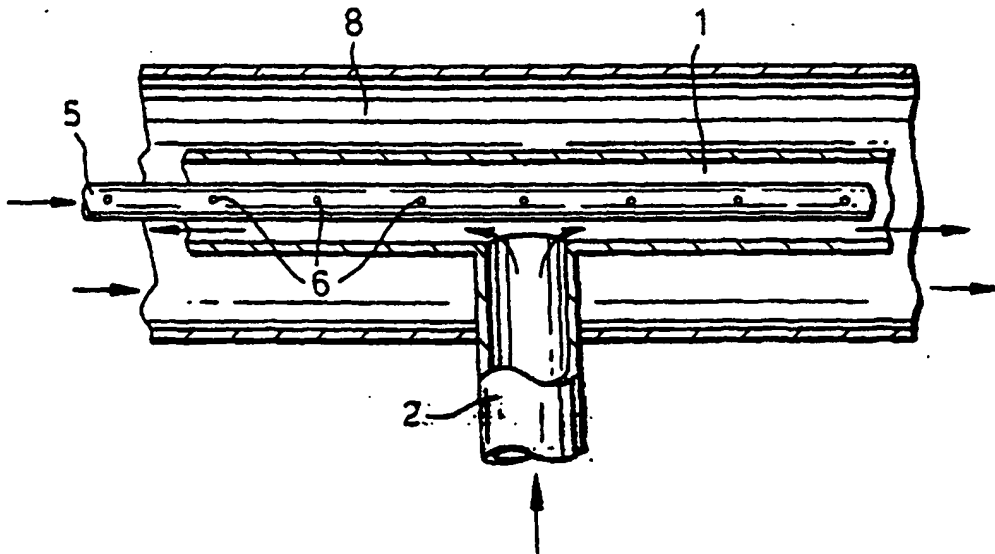


Fig.9.

